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# 3,3′-Dimethyl-1,1′-(butane-1,4-diyl)-diimidazolium bis(tetrafluoroborate)

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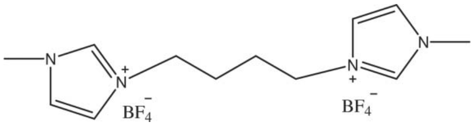
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.046; $wR$ factor = 0.155; data-to-parameter ratio = 14.8.

The title compound, $C_{12}H_{20}N_4^{2+}\cdot 2BF_4^-$, was prepared by the anion exchange of a dibromide ionic liquid with sodium tetrafluoroborate. The asymmetric unit contains one half of the imidazolium cation, which lies about an inversion centre at the mid-point of the central C—C bond of the linking butyl chain. The two planar imidazole rings (r.m.s. deviation = 0.0013 Å) are strictly parallel and separated by 2.625 (7) Å [vertical distance between the centroids of two imidazole rings], giving the molecule a stepped appearance. In the crystal structure, intermolecular C—H⋯F hydrogen bonds link the cations and anions, generating a three-dimensional network.

## Related literature

For properties and applications of ionic liquids, see: Welton (1999); Olivier & Magna (2002); Nicholas *et al.* (2004); Yu *et al.*(2007). For dicationic ionic liquids, see: Leclercq *et al.* (2007); Payagala *et al.* (2007). For bond-length data, see: Allen *et al.* (1987).



## Experimental

### *Crystal data*

$C_{12}H_{20}N_4^{2+}\cdot 2BF_4^-$
$M_r$ = 393.94
Monoclinic, $P2_1/c$
$a$ = 5.195 (1) Å
$b$ = 14.836 (3) Å
$c$ = 11.790 (2) Å
$\beta$ = 99.53 (3)°
$V$ = 896.2 (3) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 0.15 mm$^{-1}$
$T$ = 293 K
0.30 × 0.10 × 0.10 mm

### *Data collection*

Enraf–Nonius CAD-4 diffractometer
Absorption correction: $\psi$ scan (North *et al.*, 1968)
$T_{min}$ = 0.958, $T_{max}$ = 0.986
1960 measured reflections
1763 independent reflections
1125 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.019
3 standard reflections every 200 reflections
intensity decay: 1%

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.155
$S$ = 1.01
1763 reflections
119 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.20 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.19 e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H⋯$A$ | $D$—H | H⋯$A$ | $D$⋯$A$ | $D$—H⋯$A$ |
|---|---|---|---|---|
| C2—H2$A$⋯F1$^{i}$ | 0.93 | 2.50 | 3.328 (3) | 149 |
| C3—H3$A$⋯F3$^{ii}$ | 0.93 | 2.51 | 3.398 (3) | 161 |
| C4—H4$A$⋯F2$^{iii}$ | 0.93 | 2.46 | 3.272 (3) | 146 |
| C4—H4$A$⋯F3$^{iii}$ | 0.93 | 2.45 | 3.326 (3) | 158 |

Symmetry codes: (i) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x+1, y, z$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2792).

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# supporting information

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## 3,3′-Dimethyl-1,1′-(butane-1,4-diyl)diimidazolium bis(tetrafluoroborate)

**Hao Geng, Ling-hua Zhuang, Jian Zhang, Guo-wei Wang and Ai-lin Yuan**

### S1. Comment

Ionic liquids (ILs) are generally formed by an organic cation and a weakly coordinating anion. They have enjoyed considerable research interest in recent years because of their unique properties such as high thermal stability, non-volatility, non-flammability, high ionic conductivity, a wide electrochemical window and miscibility with organic compounds (Welton, 1999; Nicholas *et al.*, 2004; Yu *et al.*, 2007). ILs have been widely applied to several areas including catalysis, electrochemistry, separation science, as solvents for green chemistry, biology and materials for optoelectronic applications (Olivier & Magna, 2002). Geminal dicationic ionic liquids have been shown to possess superior physical properties in terms of thermal stability and volatility compared to traditional ionic liquids (ILs) (Leclercq *et al.*, 2007; Payagala *et al.*, 2007) .

We here report the crystal structure of the title compound (I).

The atom-numbering scheme of (I) is shown in Fig.1, and all bond lengths are within normal ranges (Allen *et al.*, 1987).

The imidazole ring (C2/C3/N2/C4/N1) is planar, with r.m.s. deviation 0.0013 Å. The two imidazole rings are strictly parallel.

In the crystal structure intermolecular C—H···F hydrogen bonds link the cations and anions generating a three-dimensional network. (Table 1 and Fig.2). ).

### S2. Experimental

A solution of 1,4-dibromobutane(4.3 g, 0.02 mol) in methanol(20 ml) was slowly added to a solution of 1-methylimidazole(3.28 g, 0.04 mol) in methanol(20 ml) at room temperature. The reaction mixture was then refluxed for 6 h. After evaporation of the solvent, the residue was washed with diethyl ether and dichloromethane, then dried in vacuum to obtain ionic liquid 3-methyl-1-[4-(1-methylimidazolium-3-yl) butyl]-imidazolium dibromide (a white solid ionic liquid).

A solution of above mentioned dibromide ionic liquid (3.8 g, 0.01 mol) in methanol(20 ml) was slowly added to a solution of sodium tetrafluoroborate (2.2 g, 0.02 mol) in methanol (20 ml), The reaction mixture was refluxed for 1 h. After evaporation of the solvent, the residue was washed with diethyl ether, then dried in vacuum to obtain title compound (I), 3-methyl-1-[4-(1-methylimidazolium-3-yl) butyl]- imidazolium ditetrafluoroborate(yield 94%). M.p. 95-97

Crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of a methanol solution. $^1$H NMR ($D_2O$, $\delta$, p.p.m.) 8.67 (s, 2 H), 7.43 (d, 4 H), 4.23 (s, 4 H), 3.87 (s,6 H), 1.88 (s, 4 H).

### S3. Refinement

All H atoms were positioned geometrically, with C—H = 0.93 Å, and constrained to ride on their parent atoms, with $U_{iso}(H) = xU_{eq}(C)$, where x= 1.5 for methyl H and x = 1.2 for methylene H atoms.

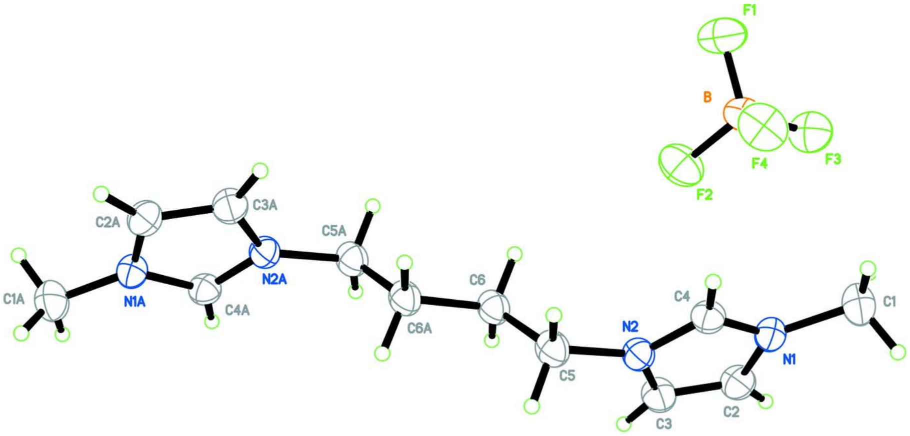

**Figure 1**

A view of the molecular structure of (I) showing the atom-numbering scheme and 30 % displacement ellipsoids .

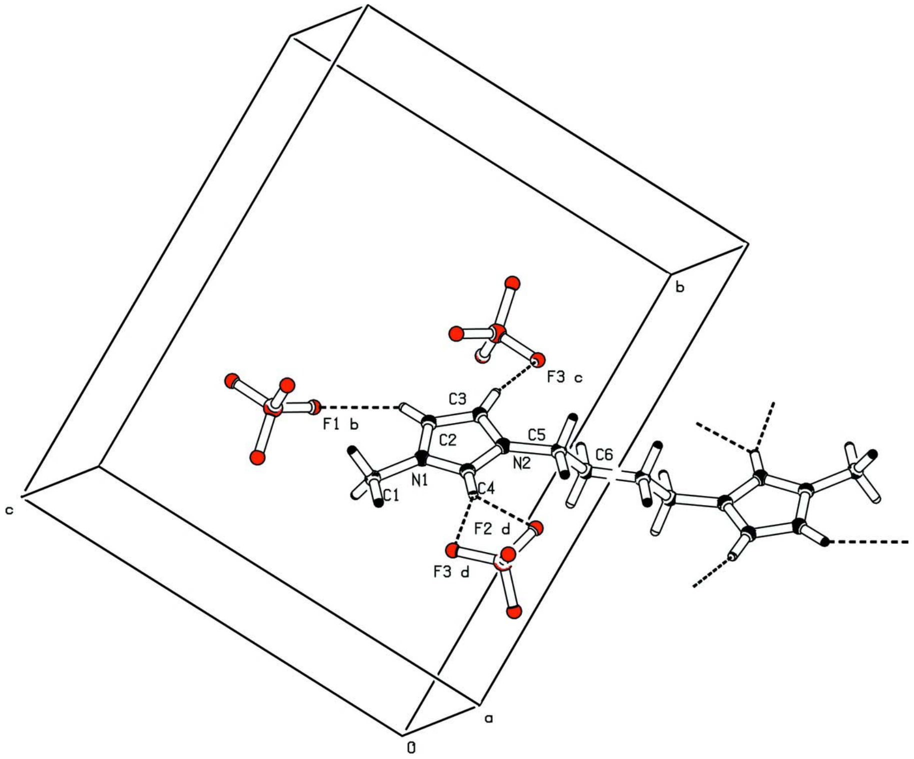

**Figure 2**

The crystal packing of (I), Hydrogen bonds are drawn as dashed lines. Symmetry codes a) x,1/2-y,1/2+z; b) 1-x,-1/2+y,3/2-z; c) 1+x,y,z

### 3,3′-Dimethyl-1,1′-(butane-1,4-diyl)diimidazolium bis(tetrafluoroborate)

*Crystal data*

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$Z = 2$
$F(000) = 404$
$D_x = 1.460$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9$–13°
$\mu = 0.15$ mm$^{-1}$
$T = 293$ K
Block, colorless
0.30 × 0.10 × 0.10 mm

*Data collection*

Enraf–Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega/2\theta$ scans
Absorption correction: $\psi$ scan (North *et al.*, 1968)
$T_{\min} = 0.958$, $T_{\max} = 0.986$
1960 measured reflections
1763 independent reflections
1125 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.019$
$\theta_{\max} = 26.0°$, $\theta_{\min} = 2.2°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 18$
$l = -14 \rightarrow 14$
3 standard reflections every 200 reflections
intensity decay: 1%

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.155$
$S = 1.01$
1763 reflections
119 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.085P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.20$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.19$ e Å$^{-3}$
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.105 (11)

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor wR and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors(gt) etc. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{\text{iso}}$*/$U_{\text{eq}}$ |
|---|---|---|---|---|
| N1 | 0.9683 (4) | 0.16123 (13) | 0.88401 (17) | 0.0515 (6) |
| C1 | 0.9656 (7) | 0.24171 (19) | 0.9557 (2) | 0.0741 (9) |
| H1A | 1.0716 | 0.2877 | 0.9296 | 0.111* |
| H1B | 1.0336 | 0.2269 | 1.0343 | 0.111* |
| H1C | 0.7897 | 0.2632 | 0.9504 | 0.111* |
| N2 | 1.0555 (4) | 0.07197 (13) | 0.75168 (16) | 0.0469 (5) |
| C2 | 0.8390 (5) | 0.08211 (17) | 0.8951 (2) | 0.0569 (7) |
| H2A | 0.7331 | 0.0695 | 0.9494 | 0.068* |

| | | | | |
|---|---|---|---|---|
| C3 | 0.8937 (5) | 0.02637 (17) | 0.8132 (2) | 0.0549 (7) |
| H3A | 0.8334 | −0.0324 | 0.8002 | 0.066* |
| C4 | 1.0970 (5) | 0.15315 (16) | 0.7964 (2) | 0.0488 (6) |
| H4A | 1.1997 | 0.1975 | 0.7706 | 0.059* |
| C5 | 1.1592 (5) | 0.03798 (17) | 0.6510 (2) | 0.0544 (7) |
| H5A | 1.2626 | −0.0156 | 0.6726 | 0.065* |
| H5B | 1.2728 | 0.0832 | 0.6261 | 0.065* |
| C6 | 0.9446 (5) | 0.01564 (17) | 0.55255 (19) | 0.0529 (7) |
| H6A | 0.8367 | 0.0685 | 0.5327 | 0.063* |
| H6B | 0.8352 | −0.0315 | 0.5761 | 0.063* |
| B | 0.5724 (6) | 0.3204 (2) | 0.6816 (3) | 0.0585 (8) |
| F1 | 0.4655 (4) | 0.37487 (13) | 0.59228 (16) | 0.0888 (7) |
| F2 | 0.5357 (3) | 0.23068 (11) | 0.65187 (17) | 0.0857 (6) |
| F3 | 0.4510 (3) | 0.33750 (12) | 0.77629 (15) | 0.0795 (6) |
| F4 | 0.8355 (3) | 0.33695 (11) | 0.70959 (16) | 0.0822 (6) |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| N1 | 0.0566 (13) | 0.0546 (13) | 0.0433 (11) | 0.0030 (10) | 0.0081 (10) | −0.0032 (9) |
| C1 | 0.090 (2) | 0.0667 (19) | 0.0645 (17) | 0.0065 (16) | 0.0092 (16) | −0.0171 (15) |
| N2 | 0.0506 (12) | 0.0452 (11) | 0.0472 (10) | −0.0001 (9) | 0.0144 (9) | 0.0006 (9) |
| C2 | 0.0621 (17) | 0.0584 (16) | 0.0546 (14) | −0.0007 (13) | 0.0224 (13) | 0.0061 (12) |
| C3 | 0.0637 (17) | 0.0472 (14) | 0.0585 (15) | −0.0084 (12) | 0.0233 (13) | 0.0030 (12) |
| C4 | 0.0503 (14) | 0.0465 (14) | 0.0503 (13) | −0.0034 (11) | 0.0103 (11) | 0.0029 (11) |
| C5 | 0.0552 (15) | 0.0531 (14) | 0.0592 (15) | 0.0022 (12) | 0.0221 (12) | −0.0017 (12) |
| C6 | 0.0595 (16) | 0.0468 (14) | 0.0565 (15) | −0.0010 (11) | 0.0216 (13) | −0.0020 (11) |
| B | 0.0488 (17) | 0.0561 (18) | 0.075 (2) | −0.0012 (14) | 0.0230 (15) | 0.0105 (16) |
| F1 | 0.0884 (14) | 0.0919 (13) | 0.0900 (13) | 0.0186 (10) | 0.0262 (10) | 0.0321 (11) |
| F2 | 0.0812 (12) | 0.0622 (11) | 0.1163 (15) | −0.0155 (9) | 0.0239 (11) | −0.0018 (10) |
| F3 | 0.0691 (11) | 0.0908 (13) | 0.0856 (12) | 0.0016 (9) | 0.0330 (9) | 0.0107 (9) |
| F4 | 0.0492 (10) | 0.0840 (13) | 0.1164 (15) | −0.0131 (9) | 0.0228 (9) | 0.0000 (10) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| N1—C4 | 1.326 (3) | C4—H4A | 0.9300 |
| N1—C2 | 1.369 (3) | C5—C6 | 1.507 (3) |
| N1—C1 | 1.465 (3) | C5—H5A | 0.9700 |
| C1—H1A | 0.9600 | C5—H5B | 0.9700 |
| C1—H1B | 0.9600 | C6—C6$^{i}$ | 1.522 (4) |
| C1—H1C | 0.9600 | C6—H6A | 0.9700 |
| N2—C4 | 1.318 (3) | C6—H6B | 0.9700 |
| N2—C3 | 1.375 (3) | B—F1 | 1.370 (4) |
| N2—C5 | 1.472 (3) | B—F4 | 1.374 (3) |
| C2—C3 | 1.337 (3) | B—F2 | 1.381 (4) |
| C2—H2A | 0.9300 | B—F3 | 1.394 (4) |
| C3—H3A | 0.9300 | | |

| | | | |
|---|---|---|---|
| C4—N1—C2 | 108.4 (2) | N1—C4—H4A | 125.5 |
| C4—N1—C1 | 125.3 (2) | N2—C5—C6 | 112.0 (2) |
| C2—N1—C1 | 126.3 (2) | N2—C5—H5A | 109.2 |
| N1—C1—H1A | 109.5 | C6—C5—H5A | 109.2 |
| N1—C1—H1B | 109.5 | N2—C5—H5B | 109.2 |
| H1A—C1—H1B | 109.5 | C6—C5—H5B | 109.2 |
| N1—C1—H1C | 109.5 | H5A—C5—H5B | 107.9 |
| H1A—C1—H1C | 109.5 | C5—C6—C6$^{i}$ | 111.3 (3) |
| H1B—C1—H1C | 109.5 | C5—C6—H6A | 109.4 |
| C4—N2—C3 | 108.2 (2) | C6$^{i}$—C6—H6A | 109.4 |
| C4—N2—C5 | 125.3 (2) | C5—C6—H6B | 109.4 |
| C3—N2—C5 | 126.4 (2) | C6$^{i}$—C6—H6B | 109.4 |
| C3—C2—N1 | 107.2 (2) | H6A—C6—H6B | 108.0 |
| C3—C2—H2A | 126.4 | F1—B—F4 | 109.8 (2) |
| N1—C2—H2A | 126.4 | F1—B—F2 | 110.6 (3) |
| C2—C3—N2 | 107.3 (2) | F4—B—F2 | 108.9 (2) |
| C2—C3—H3A | 126.3 | F1—B—F3 | 109.2 (2) |
| N2—C3—H3A | 126.3 | F4—B—F3 | 109.8 (3) |
| N2—C4—N1 | 108.9 (2) | F2—B—F3 | 108.5 (2) |
| N2—C4—H4A | 125.5 | | |

| | | | |
|---|---|---|---|
| C4—N1—C2—C3 | 0.4 (3) | C5—N2—C4—N1 | 178.3 (2) |
| C1—N1—C2—C3 | −179.9 (2) | C2—N1—C4—N2 | −0.3 (3) |
| N1—C2—C3—N2 | −0.3 (3) | C1—N1—C4—N2 | −180.0 (2) |
| C4—N2—C3—C2 | 0.2 (3) | C4—N2—C5—C6 | −117.0 (3) |
| C5—N2—C3—C2 | −178.0 (2) | C3—N2—C5—C6 | 60.9 (3) |
| C3—N2—C4—N1 | 0.1 (3) | N2—C5—C6—C6$^{i}$ | 177.6 (2) |

Symmetry code: (i) −*x*+2, −*y*, −*z*+1.

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C2—H2*A*···F1$^{ii}$ | 0.93 | 2.50 | 3.328 (3) | 149 |
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| C4—H4*A*···F3$^{iv}$ | 0.93 | 2.45 | 3.326 (3) | 158 |

Symmetry codes: (ii) *x*, −*y*+1/2, *z*+1/2; (iii) −*x*+1, *y*−1/2, −*z*+3/2; (iv) *x*+1, *y*, *z*.